Solar Energy Conversion with Ordered, Molecular, Light Harvesting Arrays

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ABSTRACT

The objective of the research is to identify, explore, evaluate, and develop non-conventional solar electric technologies capable of making a breakthrough in the production of low cost electricity from sunlight. Our approach is to utilize recently synthesized linear, semi-rigid arrays of porphyrinic compounds as antennae and charge transport carriers in organic solar cells of the sandwich type: SnO_2/porphyrin array/hole transport material/M. The porphyrinic complex has been modified at the molecular level to optimize light absorption, surface binding, and charge transfer. Here we describe initial experimental studies of such solar cells and a discussion of the potential advantages of this approach with theoretical efficiencies that could be expected.

1. Introduction

Recent advances in organic synthesis have allowed the preparation of linear, semi-rigid light harvesting arrays based upon porphyrinic pigments linked by phenyl-ethyne spacers [1,2]. Electronic coupling through the phenyl-ethyne linkages is small and the absorption spectrum of the arrays is well modeled as a summation of the individual porphryinic pigments. Picosecond $^1P*$ → ^1P energy (excitonic) transfer occurs within the pigments in these arrays that affords nearly quantitative energy transfer over long distances. Both through space and through bond energy transfer mechanisms have been identified. Intermolecular hole hopping in the one electron oxidized form of these arrays occurs on a time scale to fast to be measured by epr spectroscopy [1].

These facts bring up the intriguing possibilities for utilizing these arrays in regenerative solar cells, Fig. 1 [3]. In the simplest case one end of a linear array can be attached to the surface of a planar wide band gap semiconductor. Light excitation of pigments in the arrays would then lead to $^1P*$ → ^1P energy transfer along the arrays. An excited pigment near the semiconductor surface could then inject an electron into the

Figure 1. An array consisting of three porphyrins designed to transfer energy and holes toward opposite electrodes in a solar cell.

semiconductor. The oxidized pigment is reduced by the adjacent pigment, P^+ → P, and is vectorially translated toward the counter electrode and a hole transport material. Figure 1 shows an example of a three-porphyrin array anchored to a tin oxide electrode [3].

Below we describe our initial results designed to optimize the interfacial surface chemistry. Preliminary energy conversion studies are reported as well as a discussion of the efficiencies that can be reasonably expected with this approach.

2. Research Results and Discussion

The first generation of these solar cells will be chemically bound to the surface of a metal oxide semiconductor surface. This interfacial chemistry is expected to affect the solar cell stability, electron transfer kinetics, and the light-to-electrical energy conversion efficiency of the solar cell. We have synthesized a series of porphyrin compounds that vary only in the nature of the surface linker group, Fig. 2, and have quantified their binding to commercially available tin oxide glass. The porphyrins are abbreviated herein with a P, the central metal, and the surface linker. For clarity the Mg substituted porphyrin with a carboxylic acid binding group, $MgPCO_2H$, is emphasized as a representative example.
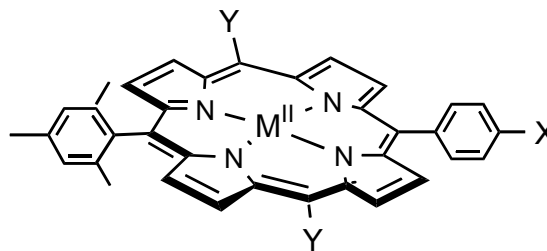

Figure 2. Porphyrins studied where X = CO_2H or OH M is Zn or Mg, and Y is mesityl.

Porphyrin binding to SnO_2 from tetrahydrofuran solutions was quantified by electrochemical and spectroscopic techniques. The maximum surface coverage observed was 7 x 10^{-11} mol/cm^2. A crude model where ~ 14 Å spheres are tightly packed on a planar substrate yields a monolayer coverage of 10^{-10} mol/cm^2 close to what is experimentally observed. Analysis of this data with the Langmuir model allows adduct formation constants of 10^5 – 10^4 M^{-1} to be abstracted. The binding constants and the limiting surface coverages for the phosphonate and carboxylic acid terminated dyes were within experimental error the same. The OH terminated porphyrins gave irreproducibly low surface coverages and this surface linker was abandoned. Carboxylic acid terminated porphyrins were found to desorb from the tin oxide surface when
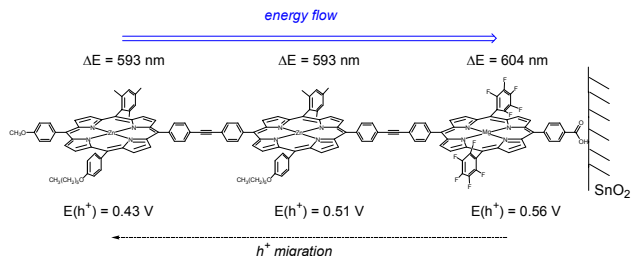
placed in neat tetrahydrofuran studies for a few hours. No significant binding was observed for porphyrins without an –OH or –CO$_2$H group for surface binding.

The solar energy conversion efficiency of ZnPCO$_2$H/SnO$_2$ was quantified in wet regenerative sandwich cells with a Pt counter electrode. Both 0.5 M I$^-$/0.05 M I$_2$ acetonitrile electrolytes or 0.5 M hydroquinone/0.05 M quinone aqueous electrolytes were studied. The limited solubility of ZnPCO$_2$H in these electrolytes allowed meaningful measurements to be made. The absorptance spectra of the ZnPCO$_2$H/SnO$_2$ agree well with the photocurrent action spectra. For a large number of samples with porphyrins that have a -CO$_2$H binding group, we typically find that 10 - 30% of the absorbed photons are converted to electrons in the external circuit. Such high photocurrent efficiencies imply efficient excited state injection into the semiconductor and regeneration by the electron donor in solution.

The solar cells displayed negligible open circuit photovoltages, V_{oc} < 10 mV, and hence extremely low power conversion efficiencies, η < 10^{-5}. We have attributed this to the highly conductive nature of the tin oxide glass and the corresponding thin space charge layer. Indeed when a layer of undoped titanium dioxide was deposited on the tin oxide prior to porphyrin binding, a large increase in V_{oc} was realized. Figure 3 shows *i*-V data measured with *quasi-monochromatic light* irradiance. The efficiency under simulated sunlight conditions was much lower, due largely to the poor light harvesting of a porphyrin monolayer on a planar surface. The light harvesting is expected to increase dramatically with longer arrays as is discussed further below.
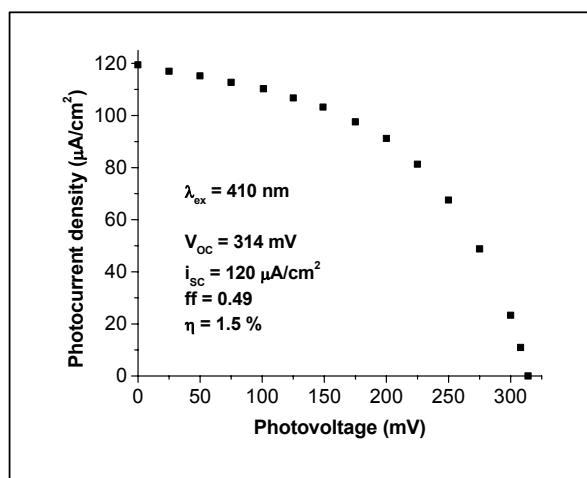

Figure 3. Current-voltage data for MgPCO$_2$H with 410 nm light excitation.

Long arrays comprised of many pigments will increase the light harvesting efficiency of the solar cells. The first generation of arrays under study has a ZnP terminal group with about 6 additional porphyrins, each of which has two appended perylene dyes. The absorption spectra of the ZnP-perylene units are known,

Fig. 4 [4-13]. The absorption spectra of porphyrins have an intense Soret band near 410 nm with a molar extinction coefficient of ε = 400,000 M^{-1} · cm^{-1} and weaker Q bands at lower energy. Perylene has an extinction coefficient of 32,000 M^{-1} · cm^{-1}. However, the absorption is polarized and since the arrays are aligned perpendicular to the electrode surface only half of the incident light will be absorbed. The electronic coupling between the porphyrins (and perylenes) is sufficiently weak that the absorption spectrum of the array is simply a linear sum of the individual porphyrin-perylene contributions [1,5,10]. This fact allows us to calculate the light harvesting efficiency for many naturally occurring and synthetic porphyrinic complexes assembled in arrays of variable length and packing density of the semiconductor surface. Details of these calculations will be included in the presentation.

Integrating the fraction of AM 1.5 light absorbed by an array allows the maximum photocurrent density to be calculated, Fig. 4. This calculation assumes that every absorbed photon is converted to an electron in the external circuit. For this assumption to be correct with the arrays in hand, the energy transfer (exciton) quantum yield from the perylenes to the porphyrins must be one, the energy transfer (exciton) quantum yield between the ZnP's to the surface bound porphyrin must be one, the injection yield from the
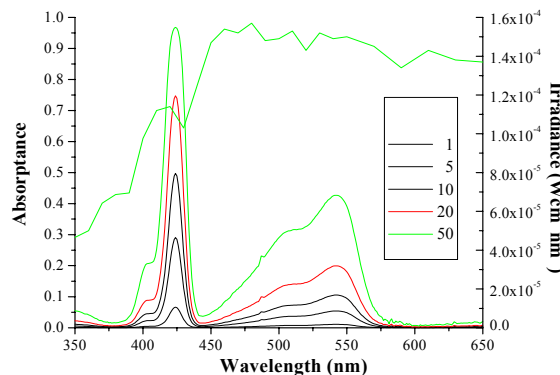

Figure 4. The calculated absorptance of porphyrin-bisperylene arrays with the indicated number of pigments in the array assuming that an array occupies 115 Å^2 on a planar electrode. Superimposed on the spectra are is the AM 1.5 solar spectrum.

excited porphyrin to the semiconductor must be one, and the oxidized array must be regenerated with a quantum yield of one with no recombination of the injected electron and the oxidized array or electron donor(s). With these assumptions and optimized fill factors and V_{oc}, global efficiencies of 2.5% are theoretically possible on a planar surface. Significant improvements in efficiency will be realized with alternative arrays that harvest a larger fraction of sunlight.

A more realistic assessment of the photocurrent density would take into account the real efficiency for energy and electron transfer in the arrays. The efficiency can be estimated using the known energy transfer rate constants measured for related arrays in fluid solution. The efficiency of energy migration to the terminal ZnPCO$_2$H site can be

calculated simply as a function of the length of the array and whether a perylene unit or a porphyrin absorbs a photon. Since the * $ZnPCO_2H$ singlet state is a potent reductant, ~ -1.0 V vs Ag/AgCl, quantitative electron injection can be reasonably assumed. Using the kinetic analysis described by Donahoe et al [2] with experimentally determined rate constants from arrays in fluid solution [1,5-11], we calculate that the injection yield for the 20th porphyrin in a 20-porphyrin array is 80%. Therefore, based on a kinetic analysis the photocurrent densities should not decrease dramatically with arrays of 20 pigments and less. This point will be elaborated upon in the presentation.

3. Conclusions

A new approach for solar energy conversion based upon ordered molecular light harvesting arrays has been introduced. The approach is new but shares some similarities with organic and dye-sensitized solar cells. Optimization of the semiconductor material and the surface linkage chemistry has been reported as well as preliminary energy conversion data. Calculated global efficiencies of a few percent can be realized with arrays that have already been reported in the literature.

4. Acknowledgements

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